

SUPERMICROCELLULAR FOAMED MATERIALS

This is a divisional of copending application Ser. No. 07/682,116 filed on Apr. 5, 1991, now U.S. Pat. No. 5,158,986.

INTRODUCTION

This invention relates generally to foamed materials, preferably foamed plastic materials, and to techniques for making and using such materials, and, more particularly, to the use of supercritical fluids for producing supermicrocellular foamed materials which can achieve a relatively wide range of material densities and a large number of extremely small voids or cells per unit volume therein.

BACKGROUND OF THE INVENTION

Techniques for making conventional foamed materials, such as foamed polymer plastic materials, have been well known for many years. Standard techniques for such purpose normally use chemical or physical blowing agents. The use of chemical agents is described, for example, by Lacallade in the text, "Plastics Engineering," Vol. 32, June 1976 which discusses various chemical blowing agents, which agents are generally low molecular weight organic compounds which decompose at a critical temperature and release a gas (or gases) such as nitrogen, carbon dioxide, or carbon monoxide. Techniques using physical agents include the introduction of a gas as a component of a polymer charge or the introduction of gases under pressure into molten polymer. Injection of a gas into a flowing stream of molten plastic is described, for example, in U.S. Pat. No. 3,796,779 issued to Greenberg on Mar. 12, 1976. Such earlier used and standard foaming processes produce voids or cells within the plastic materials which are relatively large, e.g., on the order of 100 microns, or greater, as well as relatively wide ranges of void fraction percentages e.g., from 20%-90% of the parent material. The number of voids per unit volume is relatively low and often there is a generally non-uniform distribution of such cells throughout the foamed material. Such materials tend to have relatively low mechanical strengths and toughness and there is an inability to control the dielectric constant thereof.

In order to improve the mechanical properties of such standard cellular foamed materials, a microcellular process was developed for manufacturing foamed plastics having greater cell densities and smaller cell sizes. Such a process is described, for example, in U.S. Pat. No. 4,473,665 issued on Sep. 25, 1984 to J. E. Martini-Vredensky et al. The improved technique provides for presaturating the plastic material to be processed with a uniform concentration of a gas under pressure and the provision of a sudden induction of thermodynamic instability in order to nucleate a large number of cells. For example, the material is presaturated with the gas and maintained under pressure at its glass transition temperature. The material is suddenly exposed to a low pressure to nucleate cells and promote cell growth to a desired size, depending on the desired final density, thereby producing a foamed material having microcellular voids, or cells, therein. The material is then quickly further cooled, or quenched, to maintain the microcellular structure.

Such a technique tends to increase the cell density, i.e., the number of cells per unit volume of the parent

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material, and to produce much smaller cell sizes than those in standard cellular structures. The microcellular process described tends to provide cell sizes that are generally smaller than the critical sizes of flaws that preexist in polymers so that the densities and the mechanical properties of the materials involved can be controlled without sacrificing the mechanical properties of some polymers, such as the mechanical strength and toughness of the polymer. The resulting microcellular foamed materials that are produced, using various thermoplastics and thermosetting plastics, tend to have average cell sizes in the range of 3 to 10 microns, with void fractions of up to 50% of the total volume and maximum cell densities of about one billion (10^9) voids per cubic centimeter of the parent material.

Further work in producing microcellular foamed plastic material is described in U.S. Pat. No. 4,761,256 issued on Aug. 2, 1988 to Hardenbrook et al. As set forth therein, a web of plastic material is impregnated with an inert gas and the gas is diffused out of the web in a controlled manner. The web is reheated at a foaming station to induce foaming, the temperature and duration of the foaming process being controlled prior to the generation of the web to produce the desired characteristics. The process is designed to provide for production of foamed plastic web materials in a continuous manner. The cell sizes in the foamed material appear to lie within a range from 2 to 9 microns in diameter.

It is desirable to obtain improved foamed materials which will provide even smaller cell sizes, e.g., 1.0 micron or less, and much higher cell densities as high as several thousand trillions of voids per cubic centimeter, i.e., on the order of 10^{15} , or so, voids per cubic centimeter of the parent material, for example. Such materials should also have a capability of providing a wide range of void fraction percentages from very high void fractions (low material densities) up to 90%, or more, to very low void fractions (high material densities) down to 20%, or less.

Further, it is desirable to be able to produce microcellular plastics at or near ambient temperature, so as to eliminate the need to heat the plastic during the process thereby simplifying the manufacturing process. Moreover, it is further desirable to increase the speed at which a fluid is dissolved in a polymer so that the overall time of the foaming process can be significantly reduced so as to increase the rate of production of the foamed material.

No processes used or proposed for use to date have been able to provide foamed materials having such extremely small cell sizes, such extremely high cell densities and such a wide range of material densities that provide improved material characteristics. Nor have techniques been proposed to obtain such materials at ambient temperature and at increased production rates.

BRIEF SUMMARY OF THE INVENTION

In accordance with the invention, supermicrocellular foamed materials are formed by using supercritical fluids, i.e., gases in their supercritical state, which supercritical fluids are supplied to the materials to be foamed. The supercritical fluid is used as the foaming agent in a parent material, preferably, for example, in a polymer plastic material. A relatively high density supercritical fluid made at a relatively low temperature and a relatively high pressure is used to saturate the polymer without the need to raise the saturation temperature of the process to the melting point of the polymer.

While the mechanism for achieving saturation is not fully understood in detail, it is believed that the supercritical fluid (as a solute) is initially dissolved in the polymer material (as a solvent) until the concentration percentage of supercritical fluid in the polymer reaches a reasonable level, e.g., perhaps about 10% to 40%. At some percentage level then, it is believed that supercritical fluid then tends to act as a solvent and the polymer tends to act as a solute. However, whether the supercritical fluid and polymer act as solvents or solutes during the process, at some time following the introduction of supercritical fluid into the polymer, an effectively saturated solution of the fluid and the polymer is produced. Although the aforesaid description is believed to be a reasonable theoretical explanation of what occurs during the process involved, the invention is not be construed as requiring that such specific process necessarily occurs in the manner so described.

When the fluid/polymer solution contains a sufficient amount of supercritical fluid therein at a suitably selected temperature and pressure, the temperature and/or pressure of the fluid/polymer system is rapidly changed to induce a thermodynamic instability and a foamed polymer is produced. The resulting foamed material can achieve a cell density of several hundred trillions of voids per cubic centimeter and average void or cell sizes of less than 1.0 micron, in some cases less than 0.1 micron. Moreover, in accordance with the invention, the foaming of such materials can in some cases be achieved at ambient (room) temperature conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention can be described in more detail with the help of the following drawings wherein

FIGS. 1 and 1A depict graphs of the pressure vs. specific volume relationship showing the region in which a supercritical state is achieved for carbon dioxide;

FIG. 1B depicts a graph of the pressure vs. temperature relationship showing the region in which a supercritical state is achieved for carbon dioxide;

FIG. 2 depicts a chart of critical temperatures and critical pressures required for placing various materials in their supercritical fluid states;

FIG. 3 depicts a diagrammatic view of an exemplary system for forming supermicrocellular foamed materials in accordance with the invention;

FIGS. 4 and 5 depict graphs of pressure vs. volume relationships helpful in understanding an exemplary method of the invention for an ideal and for an actual operation of the system of FIG. 3 when using carbon dioxide;

FIGS. 6, 7, 8, 9, 10, and 11 depict microphotographs showing typical cross-section views of the cells produced in various supermicrocellular foamed materials in accordance with the invention (note the micron scales indicated in the figures);

FIG. 12 depicts bar graphs of the average cell sizes produced for various supermicrocellular foamed polymer plastic materials formed in accordance with the invention under substantially the same exemplary conditions;

FIG. 13 depicts bar graphs of the average cell densities produced for the various supermicrocellular foamed polymer plastic materials shown in FIG. 12 formed under substantially the same exemplary conditions;

FIG. 14 depicts a continuous system using extrusion techniques for providing sheets of foamed materials in accordance with the invention;

FIG. 15 depicts an alternative continuous system using extrusion techniques in accordance with the invention;

FIG. 16 depicts a further alternative continuous system using extrusion techniques in accordance with the invention;

FIG. 17 depicts a system in which the foaming of a material and the forming of an article therefrom can take place in accordance with the invention; and

FIG. 18 depicts an injection molding system in accordance with the invention in which the time required for saturation of a material by a supercritical fluid is greatly reduced from that normally required for microcellular foaming.

A supercritical fluid can be defined as a material which is maintained at a temperature which exceeds a critical temperature and at a pressure which exceeds a critical pressure so as to place the material in a supercritical fluid state. In such state, the supercritical fluid has properties which cause it to act, in effect, as both a gas and a liquid. Thus, in the supercritical state, such a fluid has the solvent characteristics of a liquid, but the surface tension thereof is substantially less than that of a liquid so that the fluid can diffuse much more readily into a solute material, as in the nature of a gas.

For example, it is known that carbon dioxide (CO_2) can be placed in a supercritical state when its temperature exceeds 31°C . and its pressure exceeds 1100 psi. FIGS. 1 and 1A, for example, depict curves 10 and 12 of pressure vs. specific volume (FIG. 1) and temperature vs. specific entropy (FIG. 1A) for carbon dioxide. When the pressure is above 1100 psi and the temperature is above 31°C . (curve 10A) exemplified by the shaded region 11 of FIG. 1, and when the temperature is above about 31°C . and the pressure is above 1100 psi (curve 12A) exemplified by the shaded region 13 of FIG. 1A, carbon dioxide is provided in its supercritical state. As depicted another way, FIG. 1B shows the pressure vs. temperature relationship for CO_2 in which such critical pressure (1100 psi) and critical temperature (31°C .) are depicted so as to define the supercritical state by the shaded region 14.

The chart of FIG. 2 depicts the critical temperatures and pressures for various known exemplary materials, above which values such materials are placed in their supercritical fluid states.

FIG. 3 shows a diagrammatic view of an exemplary system for use in forming supercritical foamed materials in accordance with the invention. As can be seen therein, a source of carbon dioxide in a non-critical state is provided from a pressurized CO_2 cylinder 20 in which CO_2 is maintained at a pressure and temperature below the above discussed critical values. The CO_2 therein is supplied through conduit 21 via a high-pressure valve 22 to a high pressure chamber 23. The temperature of the chamber can be controlled, for example, by placing the chamber in a temperature controlled enclosure 24. A material 25, such as a polymer plastic material, is placed within chamber 23. The temperature of the chamber is controlled to be set at a selected initial temperature level.

In order to understand the process of the invention for providing a supercritical fluid, such as CO_2 in its supercritical state, to chamber 23 for use in producing a foamed material, it is helpful to consider the pressure-

of an exemplary cross-section thereof is shown in FIG. 11 at a magnification of 2000 X.

The bar diagrams depicted in FIGS. 12 and 13 show the correlation between average cell sizes and cell densities for the above discussed exemplary foamed materials. In the figures, the bars as related to each material are so designated in each case and, as can be seen, generally the smaller the cell sizes obtained the greater the cell densities that can be achieved.

While the producing of a supercritical fluid for use in the process of the invention is performed in the above particular examples at a temperature of 43° C. and at pressures of 1500 psi or 3000 psi, such temperatures can range from about 35° C. to about 45° C., or higher, and such pressures can range from about 1400 psi to about 6000 psi, or more. The supercritical fluid should have a relatively high density, e.g., for supercritical CO₂ fluid a density of about 0.016 moles per cubic centimeter to about 0.022 moles per cubic centimeter can be used.

Although the technique described above with reference to FIG. 3 is in effect a batch processing technique, foamed materials can also be made using a continuous process in which polymer plastic pellets or sheets are used. FIG. 14, for example, depicts one such continuous technique using a co-rotating twin screw extruder of a type well-known to those in the art for supplying a sheet of polymer to a chamber 38 for foaming of the polymer using a supercritical fluid.

As seen in the diagram of FIG. 14, an extruder barrel 30 having a plurality of barrel heaters 31 has a polymer material, e.g., in the form of polymer pellets, supplied thereto via a hopper 32. Extruder barrel 30 contains a co-rotating meshing twin screw assembly 33 for extruding polymer plastic material to a sheet die 34. A continuous sheet of polymer material is thereby supplied to an arrangement 36 of rollers held at a substantially constant temperature. A motor 37 is used to control the position of roller 35 so as to control in turn the residence time of the polymer sheet in chamber 38 by controlling the length of the sheet resident in the chamber. The roller system 36 is positioned within a chamber 38 to which is supplied a supercritical fluid from a source 39 thereof. For example, a source 39 of CO₂ in a gaseous form supplies CO₂ gas to a compressor 40, the temperature of the gas and the pressure at the compressor being controlled to place the CO₂ in its supercritical state when it is supplied to chamber 38.

As the sheet of polymer plastic travels through the roller system 36 at a selected speed, e.g., at a linear space of about 1.0 inch/second, the supercritical fluid and the polymer form a fluid/polymer system, sufficient fluid being supplied so that the sheet is effectively saturated with fluid as it leaves chamber 38. The saturated sheet of polymer emerges from chamber 38 into a foaming chamber 41 via a suitable dynamic pressure seal 42 and thence through a pair of chilled rollers 43. The drop in pressure occurring from the pressure in chamber 38 to the pressure in chamber 41, e.g., ambient pressure, as the fluid/polymer sheet exits through the dynamic seal 42 to the chilled rollers 43 causes a nucleation of cells within the fluid/polymer material which cellular nucleation is maintained at the chilled rollers 43. The fluid/polymer sheet material is then heated by passing the sheet adjacent foaming heaters 44, the time of residence therethrough being controlled by changing the length of the sheet resident in chamber 41 adjacent heaters 44 using a motor 45. The increase in temperature of the fluid/polymer material causes the nucleated cells to

expand so that the polymer material is appropriately foamed as it leaves the region of the foaming heaters 44.

In a further optional step, the foamed material can then be annealed, e.g., for crystallization of the foamed polymer, if desired, by supplying the foamed sheet material to annealing heaters 46, the time for such annealing process being controlled by changing the length of the sheet resident adjacent heaters 46 using a motor 47. The foamed, and annealed, material can then be supplied from foaming chamber 41 to a take-up roller device 48 for storage.

An alternative continuous foaming process is depicted in FIG. 15 using the system of FIG. 14 in a somewhat different manner. As can be seen therein, a supercritical fluid is supplied to a polymer plastic material while the latter material is being extruded from extruder barrel 30, the supercritical fluid, e.g., CO_2 , being obtained from a CO_2 gas supply 50 and a compressor 51, as before. The supercritical fluid is supplied to the interior of heated extruder barrel 30 at an appropriately selected position so as to introduce the fluid into the molten polymer material. Sufficient supercritical CO_2 is supplied so as to form a molten fluid/polymer material in which the polymer is effectively saturated with supercritical fluid. The molten fluid/polymer material exits from extruder barrel 30 and is supplied to a sheet die 34. Sheet die 34 forms a sheet of such fluid/polymer material, which saturated sheet is then supplied to an arrangement 53 of chilled rollers in a foaming chamber 52. The pressure in the chamber 52 is maintained at a level lower than that at the extruder barrel exit and as the pressure drops upon entering of the fluid/polymer material into chamber 52, cell nucleation occurs within the material. The chilled rollers maintain the cell nucleation condition and the fluid/polymer material is then supplied to foaming heaters 44, where cell expansion and, thereby, completion of the foaming process is achieved. As in the system of FIG. 14, the foamed polymer material can be annealed, e.g., for crystallization of the foamed polymer if desired, by annealing heaters 46 (optional) and the annealed foamed polymer material can exit the foaming chamber for supply to a take-up device 48 via chilled rollers 54. Motors 37, 45 and 47 are used as above, to control the residence times of the sheet at the corresponding regions of chamber 52.

A further alternative embodiment of the continuous process shown in FIGS. 14 and 15 is depicted in FIG. 16, wherein a supercritical fluid, e.g., CO_2 in its supercritical state, is supplied to an extruder barrel 30, as in FIG. 15, for providing saturated extruded fluid/polymer material therefrom. The extruded material is then formed into a sheet of fluid/polymer material and supplied to a pressurized chamber 55, the pressure in which is suitably controlled by a pressure controller 59. The sheet material is supplied to an arrangement 56 of constant temperature rollers and thence exits chamber 55 via a dynamic pressure seal 57.

If the pressure in chamber 55 is maintained at substantially the same pressure as the saturation pressure of the supercritical fluid supplied by compressor 51, both cell nucleation and cell expansion occur as the fluid/polymer sheet exits via dynamic seal 57 due to the pressure drop from the pressure in chamber 55 to the lower pressure in an annealing chamber 58. The foamed polymer material is then passed through chilled rollers 60 to maintain its foamed condition and supplied to annealing heaters 46 and thence to take-up device 48, as before.

supermicrocellular structure. Accordingly, the article is both foamed and formed at room (ambient) temperature in one overall operation.

In the above disclosed embodiments, there is a finite time which is required for a polymer material to become saturated with a supercritical fluid. i.e., for a sufficient amount of supercritical fluid to be introduced into the polymer to form a fluid/polymer solution which can be appropriately foamed to provide a desired supermicrocellular foamed material. While in some cases such time can be as low as 10 minutes, e.g., when using a soft PVC material having a thickness of 1/16 inch (1.59 mm), in other cases longer times may be required depending on the thickness desired. While such embodiments can be useful in many applications, in other applications it may be desirable to reduce the time need for such purpose. For example, in order to enhance the ability to use the technique of the invention in some applications to achieve relatively high production rates for obtaining supermicrocellular formed material, it is often desirable to use much shorter saturation time periods. One technique for doing so is depicted in the system shown in FIG. 18 in which a supercritical fluid is introduced into an extrusion barrel 70, for example, for injecting the saturated material into a mold.

As can be seen in the diagrammatic presentation of FIG. 18, an extrusion barrel 70 utilizes a screw 71, with integrated mixing elements 83, of a type having irregular blades, as would be well known to those in the art, into which plastic pellets of a polymer material are introduced via a hopper assembly 72. The extrusion barrel is heated so that the pellets become plasticized and reach a molten state as they are moved by the mixing screw along the barrel 70, in a manner similar to that discussed with reference to FIGS. 14, 15 and 16. A source 82 of CO₂ gas is introduced into the extrusion barrel at a selected position along mixing screw 71 via the operation of a suitable flow control valve 73, the temperature and pressure in the extrusion barrel at that point being controlled so as to be greater than the critical temperature and pressure for converting the CO₂ in gaseous form into CO₂ in its supercritical state. The CO₂ gas may be preheated before insertion, if desired, to prevent too sudden an increase in pressure in the barrel at the higher temperature of the barrel. Alternatively, the CO₂ gas can be converted to its supercritical state externally to the extrusion barrel and supplied to the mixing screw as a supercritical CO₂ fluid.

The supercritical CO₂ fluid is mixed with the molten polymer material by the mixing screw and such mixing enhances the subsequent diffusion into, and effective saturation of supercritical CO₂ fluid in, the polymer because the contact area of the two materials being mixed is increased by the mixing process and the depth required for diffusion is decreased thereby.

Thus, the supercritical CO₂ fluid is mixed with the molten polymer by the motion of the mixing screw to aid in forming a solution. As the mixing screw rotates, it generates a two-dimensional shear field in the mixed CO₂/polymer system. The bubbles of supercritical CO₂ fluid in the polymer melt are stretched along the shear directions of the shear field. The stretched bubbles are then broken into smaller spherical shaped bubbles by the perturbation of the laminar flow which is generated by the mixing screw. The irregular blades used in the mixing screw change the orientation of the CO₂/polymer interface relative to the streamlines, which

change increases the efficiency of the laminar mixing occurring therein.

The CO₂/polymer mix is supplied to a static mixer 74 which continually changes the orientation of the CO₂/polymer interface relative to the streamlines and thereby also enhances the mixing process. Static mixers for use in an extrusion barrel are well known to the art and are made and sold commercially. The diameter of static mixer 74 should be small and the static mixer can comprise a selected number of mixer elements 75, as further discussed below.

If the diameter of the static mixer elements is too large, the flow rate of the CO₂/polymer mixture there-through is small and, consequently, the shear field generated by the static mixer elements is small. The spherical shapes of the bubbles would thereby be maintained because the surface tension would be dominant and, in effect, the surface tension would overcome the effect of the relatively small shear field. When the flow rate is too small, a static mixer is not effective for mixing the CO₂/polymer system into a solution because of such dominant surface tension. Hence, it is desirable to make the diameter of the static mixer relatively small.

The characteristic length of the static mixing which occurs in static mixer 74, i.e., the striation thickness of the mixed CO₂/polymer layers, is approximately $d/2^n$ where d is the diameter of the static mixer elements and n is the number of the mixing elements 75. Better mixing occurs when mixer elements having a small radius are used because such characteristic length of the mixing decreases as the diameter decreases, as well as when a relatively large number of mixing elements is used. The number of mixing elements and the diameters thereof can be selected so as to assure a satisfactory and adequate static mixing operation.

During the static mixing of the CO₂/polymer system, the CO₂ molecules in the bubbles also tend to diffuse somewhat into the polymer melt material which surrounds each bubble. However, the primary diffusion operation takes place in a diffusion chamber 76 into which the two-phase gas/polymer mixture is introduced. The mixture then becomes a complete single-phase solution in the diffusion chamber as the CO₂ diffuses into the polymer therein. The CO₂ concentration in the single-phase CO₂/polymer solution thereby produced is substantially uniform throughout the solution and the solution is effectively homogeneous. If the supercritical CO₂ fluid does not diffuse into and saturate the polymer uniformly and homogeneously, the foamed structure that is ultimately formed will not be uniform because the cell morphology strongly depends on the local gas concentration in the solution.

The homogeneous and uniform fluid/polymer solution in diffusion chamber 76 is then heated in a heating section 77 thereof where the solution is rapidly heated (in a typical case the temperature may rise from about 190° C. to about 245° C., in about 1.0 second, for example), so as to form nucleated cells in the saturated solution due to the thermodynamic instability which is created because of the decreased solubility of the fluid/polymer solutions at the higher temperature. The greater the decrease in solubility which occurs, the higher the cell nucleation rate and the larger the number of cells nucleated. To prevent the nucleated cells from growing in the extrusion barrel 70 a high barrel pressure is maintained. The solution with nucleated cells is then injected into a mold cavity 78 of a mold 79, the pressure in the mold cavity being controlled by

providing a counter pressure to prevent cell growth during the mold filling process. The counter pressure is provided by the insertion of air under pressure from a source 80 thereof via shut-off valve 81. Finally, cell growth occurs inside the mold cavity when the mold cavity is expanded and the pressure therein is reduced rapidly, thereby producing a pressure instability which enhances cell growth.

Accordingly, expansion of the mold provides a molded and foamed article having the small cell sizes and high cell densities desired. By using a mixing screw for providing a shear field which produces a laminar flow of the mixed materials and then by using both a static mixer having small diameter mixing elements and a selected number of such mixing elements and a diffusion chamber, saturation of the polymer material with supercritical CO₂ fluid occurs. The time period required to provide such saturation can be reduced from that required in the embodiments of the invention discussed previously so that it is possible to achieve continuous operation at relatively high production rates that would not be possible when longer saturation times are needed.

The provision of extremely small cell sizes and high densities thereof in a foamed polymer material, as achieved when using supercritical fluids to provide the foaming operation, as described with reference to the above embodiments of the inventions brings about substantially improved properties for the foamed materials obtained, particularly compared with previous standard cellular or microcellular foamed materials. Thus, the mechanical strengths and toughness thereof are substantially greater, even when the weight of the material (i.e., the material density) is considerably reduced. Moreover, less polymer material is used in the process and, accordingly, material is conserved and the costs thereof are reduced.

While the embodiments of the invention described above represent preferred embodiments thereof, modifications thereof and still other embodiments may occur to those in the art within the spirit and scope of the invention. Hence, the invention is not to be construed as limited to the specific embodiments thereof described above, except as defined by the appended claims.

What is claimed is: